



PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: : Docket: ANO 6119/3156
PERSSON, et al. : Examiner: Peter Chin
Serial No. 10/007,885 : Group Art Unit: 1731
Filing Date: November 5, 2001 :
For: SILICA-BASED SOLS :
:

Assistant Commissioner for Patents
Washington, D.C. 20231

DECLARATION UNDER 37 C.F.R. §1.132

Sir:

I, Marek Tokarz, do hereby declare and say that:

1. I am a citizen of Sweden residing at Håkons Gata 4, SE-442 39 Kungälv, Sweden.
2. I have a degree of M.Sc.Eng. from University Academy of Mining and Metallurgy in Krakow, Poland, and a degree of Ph.D. from University of Utah in Salt Lake City, UT, USA.
3. I am a Senior Specialist employed by Eka Chemicals AB since 1984, and since 1990 I have been involved in the development of silica-based sols for use in papermaking.
4. I am a co-inventor of U.S. Patent Application Serial No. 10/007,885 ("the present application") and I am familiar with the fields of silica-based sols and papermaking.
5. I have also read and understood the specifications of U.S. Patent Nos. 5,277,764 (Johansson et al), 5,607,552 (Andersson et al) and 6,486,216 (Keiser et al) cited in the present application.

6. The following tests, relating to the preparation of aqueous sols containing silica-based particles and evaluation of these sols by means of drainage and retention performance in papermaking, have been conducted by me or under my direct supervision:

Three standard aqueous sols containing silica-based particles were prepared by a prior art process according to the following.

762.7 g sodium water glass with a molar ratio of SiO_2 to Na_2O of 3.3 and SiO_2 content of 27.1 % by weight was diluted with water to 3000 g yielding a silicate solution (I) with a SiO_2 content of 6.9% by weight. 2800 g of this silicate or water glass solution was passed through a column filled with a strong cation exchange resin saturated with hydrogen ions. 2450 g of ion-exchanged water glass or polysilicic acid (II) with an SiO_2 content of 6.5% by weight and a pH of 2.4 was collected from the ion exchanger. 1988 g of the polysilicic acid (II) was fed into a reactor and diluted with 12.3 g water. 173.9 g of the 6.9% silicate solution (I) was then added under vigorous agitation. The resulting solution was then heated at 85°C for 60 minutes and then cooled to 20°C to provide a sol of containing silica-based particles. A similar process was used to produce additional sols using somewhat different settings.

Table 1 shows the parameters of the prior art aqueous sols containing silica-based particles.

Table 1

Sol No.	Specific Surface Area [m ² /g]	S-value [%]	Viscosity [cP]	pH	Molar Ratio $\text{SiO}_2:\text{Na}_2\text{O}$	Content of Silica [% by weight]
1a	530	29	2.2	10.2	40	7.3
1b	500	26	2.7	10.0	63	7.3
1c	690	32	1.6	9.8	35	5.4

Three additional aqueous sols containing silica-based particles were prepared by a prior art process comprising acidification of an aqueous sodium silicate solution to a pH below 4 and subsequent alkalization to a pH of at least 9:

The aqueous sodium silicate solution, which had a molar ratio SiO_2 to Na_2O of about 3.5, was acidified to a pH below 4 by means of an acid cation exchanger saturated with hydrogen ions to form a polysilicic acid. The polysilicic acid was subjected to alkalization by means of addition of an aqueous sodium silicate solution having a molar ratio SiO_2 to Na_2O of about 3.5. The degree of microgel was influenced by, inter alia, keeping the SiO_2 content during the alkalization in the range of from 4.5 to 7.0% by weight.

Table 2 shows the parameters of the prior art aqueous sols containing silica-based particles.

Table 2

Sol No.	Specific Surface Area [m^2/g]	S-value [%]	Viscosity [cP]	pH	Molar Ratio $\text{SiO}_2:\text{Na}_2\text{O}$	Content of Silica [% by weight]
1d	850	30	3.1	9.0	30	7.8
1e	850	24	5.0	9.0	45	7.4
1f	870	35	2.5	10.6	10	10.0

7. Six aqueous sols containing silica-based particles according to the invention claimed in the present application were prepared from a polysilicic acid similar to the polysilicic acid (II) according to point 6 above produced with the same ion exchange process and with an SiO_2 content of 5.46 % by weight. To 102.0 kg of the polysilicic acid was added 1.46 kg of sodium water glass with a ratio $\text{SiO}_2/\text{Na}_2\text{O}$ of 3.3 under vigorous agitation resulting in a solution with a molar ratio $\text{SiO}_2/\text{Na}_2\text{O}$ of 54.0. This solution was heat treated at 60°C for 2 h 20 min and cooled to 20°C whereupon the product was concentrated to a SiO_2 content of 15.6 % by weight. This intermediate sol product was now divided into six separate samples, a to f. Samples a to c were further alkaliised with NaOH, samples d to f with water glass, to achieve sols with a molar ratio $\text{SiO}_2/\text{Na}_2\text{O}$ between 21.5 and 34.0 and a silica content of about 15.0 % by weight.

Table 3 shows the parameters of the aqueous sols containing silica-based particles according to the invention claimed in the present application:

Table 3

Sol No.	Specific Surface Area [m ² /g]	S-value [%]	Viscosity [cP]	pH	Molar Ratio SiO ₂ :Na ₂ O	Content of Silica [% by weight]
2a	720	31	17	10.7	21.5	about 15
2b	710	30	29	10.3	28.0	about 15
2c	690	29	40	10.0	34.0	about 15
2d	680	31	20	10.7	21.5	about 15
2e	670	29	34	10.3	28.0	about 15
2f	680	29	38	10.0	33.0	about 15

Three additional aqueous sols containing silica-based particles according to the invention claimed in the present application, Sols 3, 4, 5a and 5b, were produced as follows:

A polysilicic acid (II) produced with the above ion exchange process and alkaliised with water glass to a molar ratio SiO₂/Na₂O of 54.0 as under point 6 above was heat treated at 60°C for 1 h. To 58 kg of this product was added 7.25 kg of diluted water glass with a molar ratio SiO₂/Na₂O of 3.3 and silica content 5.5 % by weight. The resulting sol of silica-based particles, Sol 3, was then concentrated.

1000 g polysilicic acid (II) with an SiO₂ content of 5.5 % by weight was mixed with 14.5 g water glass solution with an SiO₂ content of 27.1 % by weight and a molar ratio SiO₂/Na₂O = 3.3 under vigorous agitation resulting in a product with a molar ratio SiO₂/Na₂O of 51 and a silica content of 5.8 % by weight SiO₂, which was heat treated at 60°C for 1.5 h and then concentrated to a silica content of 16.7 % by weight SiO₂. 283 g of the product obtained was mixed with 33.0 g NaOH resulting in a sol of silica-based particles, Sol 4.

The general procedure used for Sol 4 was followed except that the heat treatment was carried out for 1.25 h and concentration was carried out to higher silica contents. Two sols of silica-based particles were prepared; Sol 5a and Sol 5b.

Table 4 shows the parameters of Sols 3, 4, 5a and 5b according to the invention claimed in the present application:

Table 4

Sol No.	Specific Surface Area [m ² /g]	S-value [%]	Viscosity [cP]	pH	Molar Ratio SiO ₂ :Na ₂ O	Content of Silica [% by weight]
3	760	34	9.0	10.7	24	15.2
4	720	32	14.2	10.6	21	15.2
5a	700	36	18	10.7	18	18
5b	700	37	31	10.7	18.3	20

7. Drainage performance was evaluated by means of a Dynamic Drainage Analyser (DDA), available from Akribi, Sweden, which measures the time for draining a set volume of stock through a wire when removing a plug and applying vacuum to that side of the wire opposite to the side on which the stock is present.

The stock used was based on a blend of 60 % by weight bleached birch sulphate and 40 % by weight bleached pine sulphate to which was added 30 % by weight ground calcium carbonate as a filler. Stock volume was 800 ml, consistency 0.25 % by weight and pH about 8.0. Conductivity of the stock was adjusted to 0.47 mS/cm by addition of sodium sulphate.

In the tests, silica-based sols were used in conjunction with a cationic polymer, Raisamyl 142, which is a conventional medium-high cationised starch having a degree of substitution of 0.042, which was added to the stock in an amount of 12 kg/tonne, calculated as dry starch on dry stock system. Silica-based sols described above were tested and compared with standard sols 6a and 6b. Table 5 shows the parameters of these prior art aqueous sols containing silica-based particles.

Table 5

Sol No.	Specific Surface Area [m ² /g]	S-value [%]	Viscosity [cP]	pH	Molar Ratio SiO ₂ :Na ₂ O	Content of Silica [% by weight]
6a	500	45	3.0	10.2	40	15.0
6b	880	36	2.5	11	10	10.0

The silica-based sols were added in an amount of 0.5 kg/ton, calculated as SiO₂ and based on dry stock system. The stock was stirred in a baffled jar at a speed of 1500 rpm throughout the test and chemical additions were conducted as follows: i) adding cationic starch to the stock following by stirring for 30 seconds, ii) adding silica-based sol to the stock followed by stirring for 15 seconds, iii) draining the stock while automatically recording the drainage time. Drainage times for the different silica-based sols are shown in Table 6:

Table 6

Silica-based sol	Drainage time [sec]
Sol 1a (ref.)	12.0
Sol 1b (ref.)	11.1
Sol 1c (ref.)	12.0
Sol 2d	9.7
Sol 3	9.5
Sol 4	9.4
Sol 6a (ref.)	12.0
Sol 6b (ref.)	9.8

Table 6 shows that the aqueous sols containing silica-based particles according to the invention claimed in the present application provided improved drainage times.

8. Drainage performance was evaluated according to the general procedure described under point 7 above except that the stock had a consistency of 0.3% and pH about 8.5. Retention performance was evaluated by means of a nephelometer by measuring the turbidity of the filtrate, the white water, obtained by draining the stock.

Silica-based sols according to invention claimed in the present application were tested against Sol 6a used for comparison. Table 7 shows the drainage time obtained at various dosages (kg/ton) of silica-based particles, calculated as SiO₂ and based on dry stock system. The addition of only cationic starch (12 kg/tonne, calculated as dry starch on dry stock system) resulted in a drainage time of 15.8 sec.

Table 7

Silica-based sol	Drainage time (sec) / Turbidity (NTU) at SiO ₂ dosage of				
	0.5 kg/t	1.0 kg/t	1.5 kg/t	2.0 kg/t	3.0 kg/t
Sol 6a (ref.)	11.1/ -	8.8/59	7.9/58	7.1/54	6.8/60
Sol 5a	9.0/ -	7.1/52	6.3/50	5.2/52	5.7/53
Sol 5b	8.9/ -	6.9/ -	6.3/ -	5.7/ -	6.0/ -

Table 7 shows that the aqueous sols containing silica-based particles according to the invention claimed in the present application provided improved drainage times.

9. In an Office Action mailed December 15, 2004 in respect of the present application, it is stated "since viscosity is dependent on such factors as particle size and surface area, it is obvious that since the S-values and specific surface area of the above prior art sols are within the claimed range, the prior art obviously encompasses the claimed viscosity".

In my professional opinion, it is correct that viscosity is dependent on such factors as particle size and surface area. However, I conclude that it is not correct that since the S-values and specific surface area of the above prior art sols are within the claimed range, the prior art obviously encompasses the claimed viscosity. The above tests show prior art sols of silica-based particles having S-values and specific surface areas within the claimed range but having viscosities outside the claimed range.

10. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: 13-06-2005

Name: Marek Tokarz

Marek Tokarz